

Urban Aerosol Modeling: Incorporation of an
SO₂ Photochemical Oxidation Module in AROSOL

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URBAN AEROSOL MODELING : INCORPORATION OF AN SO₂ PHOTOCHEMICAL OXIDATION
MODULE IN AROSOL

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ABSTRACT

Modules for conversion of sulfate have been included in the urban scale K-theory aerosol model, AROSOL. Two modules are included: one is an empirical first-order SO_2 conversion scheme termed EMM and the other is a series of chemical kinetic reactions based on the Carbon Bond Mechanism, termed CBM-IV. These modules can interact with two modules for the aerosol phase. One, the aerosol dynamics model (ADM), includes modules for binary nucleation of the sulfuric acid-water system and condensation of sulfuric acid on existing particles. The other is termed the lumped aerosol model (LAM) and treats sulfate as another separate component in the atmosphere. LAM is widely used in regional scale simulations. It has, however, deficiencies that may be important on the urban scale. The use of LAM and ADM with AROSOL is discussed. The use of EMM and LAM in AROSOL is illustrated with test simulations using 1982 Philadelphia Aerosol Field Study data.

It is planned to develop an "engineering" model version of AROSOL suitable for use by various Federal and State agencies for regulatory purposes. The aim is to replace the commonly applied Gaussian plume models in use today. Feasibility of porting this "engineering" model to the IBM PC-RT is discussed

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LIST OF SYMBOLS

b	coagulation rate constant, $\text{m}^3\text{sec}^{-1}$
D	solar declination angle, degrees
f_A	empirical function for annual variation of k
f_D	empirical function for diurnal variation of k
G	gravitational sedimentation velocity, m sec^{-1}
i	julian date
k	pseudo-first order SO_2 decay rate constant, sec^{-1}
K	eddy diffusivity, $\text{m}^2 \text{sec}^{-1}$
L	latitude
m	aerosol particle mass, kg
n	aersol number density function, $\# \text{m}^{-3}\text{kg}^{-1}$
R	homogeneous nucleation rate, $\# \text{m}^{-3} \text{sec}^{-1} \text{kg}^{-1}$
s	vertical terrain following coordinate
S	gaseous species sink, $\text{kg m}^{-3}\text{sec}^{-1}$
V_d	deposition velocity, m sec^{-1}
x_i	mass fraction of species i
x	horizontal Eulerian coordinate, km
y	horizontal Eulerian coordinate, km
z	vertical Eulerian coordinate, km

SECTION 1

INTRODUCTION

The adverse effects of urban air pollution are well known: increased incidence of respiratory diseases, reduced visibility, economic loss, and inadvertent weather modification, to name a few. The urban aerosol plays an important role in these adverse effects. An understanding of this role requires, among other factors, knowledge of the aerosol dynamical processes shaping the aerosol size and composition distributions. These dynamical processes include advection, dispersion, deposition, primary and secondary source input, nucleation, condensation/evaporation, and coagulation. Models for the particle size and composition distributions reflecting these dynamical processes will ultimately be necessary for development of realistic aerosol air quality regulations and control strategies. For example, the deposition pattern of particles in the lung is a function of the particle size distribution. Absorption and scattering of light by the ambient aerosol is a complex function of the composition distribution. Many of the chemical species making up the urban aerosol are produced through the interaction of complex chemical processes and the ambient aerosol, the details of which vary with particle size and composition. Therefore, the effects of pollutant emissions reduction and control are likely to be nonlinear in character and will require the detailed knowledge cited.

This project has been concerned with development of urban aerosol models which include the dynamical processes shaping the aerosol size and composition distributions. The first part of this work has involved evaluation of data bases and a K-theory model, termed AROSOL, for the super- and sub-micrometer aerosol mass concentration. Recent work has been devoted to development of computer modules for accurate description of the coagulation and condensation/evaporation processes for single component aerosols. Current work has proceeded along several lines. The data bases from the EPA Philadelphia Aerosol Field Study (PAFS) have been evaluated

and corrected for evaluation of AROSOL for sulfate aerosol modeling. Modules have been developed for inclusion in AROSOL which account for chemical conversion, nucleation, condensation, evaporation, and coagulation as a step in the extension of AROSOL to multicomponent aerosols. Work has been done on coupling the nucleation and condensation/evaporation processes to a suitable oxidant mechanism for sulfate formation. A parallel development is the derivation of a more highly parameterized model from AROSOL suitable for assessments.

SECTION 2

CONCLUSIONS

The urban scale K-theory aerosol model, AROSOL, has been extended to account for sulfate formation using an empirical first-order SO_2 conversion scheme as well as a module for a series of chemical kinetic mechanisms based on the Carbon Bond Mechanisms (CBM) . The CBM module can interact with modules for binary nucleation of the sulfuric acid-water system and condensation of sulfuric acid on existing particles. It is possible, therefore, to operate AROSOL either as a lumped sulfate model or as a model which predicts the particle size and composition distributions.

Algorithms used in AROSOL for calculation of advection and dispersion have been updated. Algorithms for calculation of vertical diffusivity have been modified to include the parameterizations of Deardorff. An algorithm for advection has been used based on the scheme of Smolarkiewicz; this scheme maintains adequately conservation and positiveness of the concentrations and is relatively fast compared to other conserving methods.

Data bases from the EPA Philadelphia Aerosol Field Study (PAFS) have been analyzed and corrected for evaluation of AROSOL for sulfate aerosol modeling.

AROSOL may be regarded as a research model for urban aerosol modeling. Most of the model runs have been carried out on the University of Texas CDC Twin Cybers, although these calculations will be shifted to a CRAY XMP now available at the University of Texas Center for High Performance Computing. It is planned to develop simplified model from AROSOL . This simplified model will be available for assessment purposes. This simplified K-theory model is anticipated to be the replacement for the commonly applied Gaussian plume models in use today. The feasibility of porting this simplified model to the IBM PC-RT is under investigation.

SECTION 3

RECOMMENDATIONS

With increasing speed and memory of computers it is feasible to carry out evaluation studies of models such as AROSOL for the aerosol size and composition distributions. As a first step, planning of field studies should be carried out for obtaining the needed field data, including emissions inventory and measurements of either the aerosol distributions or their moments. The moment of a distribution is the integral, over the range of the size parameter, of the product of the distribution and some power of the size parameter. For example, the first moment of a mass distribution of particles would be the total mass concentration of particles. Planning of such field studies implies that suitable measurement systems would be available. Therefore, while development of AROSOL continues, a parallel program for development of experimental systems for large area measurements of ambient aerosol size and composition distributions, or their moments, would be desirable. Modern developments in laser spectroscopy and remote sensing would appear to make it feasible to carry out field studies at relatively low cost that would gather information on gas concentrations and aerosol distributions on spatial scales commensurate with the urban scale simulation grids (typically 1kmx1km) . Point source measurements are always subject to local spatial and temporal fluctuations that cannot be included in any reasonable manner in numerical simulations, and such measurements are well below the feasible limits of resolution of numerical models. Even from a regulatory standpoint, the always restricted number of point measurement stations are well known to be subject to anomalous local effects which can lead to ineffective and costly regulatory actions.

The Gaussian plume model, although widely employed today for regulatory purposes throughout the United States, has well recognized and serious deficiencies. A substantial advance over the Gaussian plume model

is afforded by the conservation equation with first-order closure-- the K-theory model. For both aerosol and gaseous species modeling, it is recommended that simplified K-theory models be developed that would run with reasonable efficiency on newly available and relatively inexpensive work stations such as the IBM PC-RT.

SECTION 4

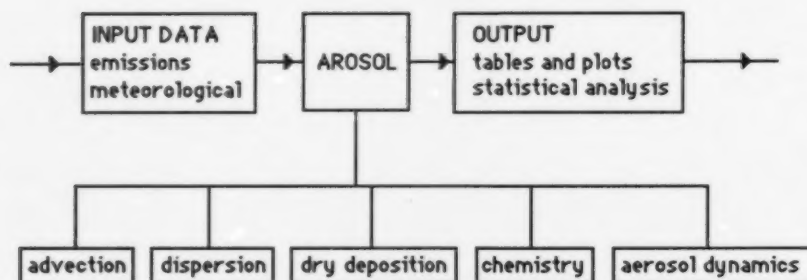
PROCEDURE

AROSOL is an urban scale K-theory model for the ambient atmospheric aerosol. It has been previously used in a number of studies including modeling total aerosol mass concentration in Maricopa County, Arizona¹ and super- and sub-micrometer aerosol mass concentration in St. Louis, Missouri using the Regional Air Pollution Study (RAPS) data base². This model has been under continuous development. The extension of the model to include secondary sulfate aerosol sources is described here. First the various components of AROSOL will be presented. This is followed by detailed discussion of the various modules available in AROSOL, including the recent work on inclusion of oxidant chemistry for the gas phase conversion of SO₂ to sulfate. The heterogeneous conversion of SO₂ in liquid aerosols will be included in modules presently under development.

GENERAL DESCRIPTION

AROSOL is a K-theory model for the ambient atmospheric aerosol. It is arranged with a number of options for inclusion of meteorological data ranging from a single measurement of wind speed and direction to time series of data on wind speed and direction and atmospheric stability. At present, the model includes no numerical meteorological driver.

The structure of AROSOL is best indicated by the schematic diagram shown below.



As indicated, data input includes emissions inventory data and meteorological data. Emissions inventory data are entered from tape or other data storage media. Meteorological data may be entered externally from data storage media or, in the case of limited meteorological data, may be entered internally through data statements. The model has provision for inferring complete wind field and stability conditions over a study area for a range of data availability from measurements at a single point to complete time series at multiple points.

Results from AROSOL simulations may be displayed in various forms including tabular data, isopleth plots, and full three dimensional plots. Modules are available for analysis of simulation results and measurement data including statistical analysis options for model evaluation as recommended by EPA as well as spectral analysis. New analytical modules will be included as available.

The various rate modules of AROSOL are indicated in the diagram above. The Eulerian grid consists of horizontal x,y UTM coordinates and a vertical sigma, s, coordinate³ for simulation of complex terrain; introduction of the s-coordinate in the code required about 20 hours (\$1000) of consultants' time. The horizontal grid is usually employed with a variable mesh with highest density in the regions of large sources. Usually, no more than the order of 14 vertical levels of variable thickness are employed. Time splitting^{4,5} is employed based on the process. The steps are ordered as first, advection, then diffusion, and finally the

aerosol dynamical and chemical processes.

The x,y boundary conditions are specified depending on the whether the wind is flowing into or out of the modeling region. For wind flowing out of the modeling region a constant flux conditions in x,y is imposed. For wind flowing into the modeling region, the appropriate pollutant variable must be imposed; these values must be set from background assumptions or actual upstream measurements. The boundary condition at the surface is discussed below under the section on dry deposition. The upper level boundary condition is usually specified by a zero flux condition at the mixing height which is specified from field data. It is possible to allow for entrainment through the upper boundary but this must be done empirically.

The rate modules indicated in the diagram above will now be discussed in order.

RATE MODULES

Advection

The advection term in the conservation equation is evaluated numerically using the iterated upstream finite difference scheme proposed by Smolarkiewicz⁶. This scheme is used because it maintains the conservation and positiveness of transported conservative species reasonably well. The scheme is also relatively fast compared to other methods with similar conservation properties. In addition the scheme is local in that the advective time change at a point is determined by the concentrations and velocities at a small number of neighboring points.

Dispersion

The vertical and horizontal diffusivity terms are handled by orthogonal collocation on finite elements. This scheme has been found to provide reasonable accuracy and efficiency in dispersion simulations⁷.

It is widely recognized that the eddy diffusivities are not fluid

properties but are functions of the dynamical state of the atmosphere. Therefore the eddy diffusivities are empirical constructs which must be specified for various atmospheric states. For all but small advective flows, horizontal diffusivity, K_H , is relatively unimportant compared to advection as a transport mechanism; this is fortunate since an adequate parameterization of this coefficient is lacking. In AROSOL, K_H is chosen as $50 \text{ m}^2/\text{sec}$. The vertical diffusivity, K_V , is often the dominant mechanism for vertical transport. K_V is calculated from the friction velocity and Monin-Obukhov length. These parameters are specified by the stability class, the ground level wind speed, the surface roughness, the height of the wind measurements, and the height of the grid cell. Atmospheric stability is based on the Pasquill atmospheric stability class. Surface roughness may be estimated from aerial photographs using known procedures². Parameterizations of K_V for stable⁸ and neutral and unstable⁹ conditions are employed.

Dry deposition

At the surface, the boundary condition is specified by parameterizations of deposition velocities. For gases, surface resistances are scaled from field data for SO_2 . For submicrometer and particulate sulfate, a parameterization due to Wesely and Shannon is used¹⁰ for the deposition velocity. Deposition velocities for supermicrometer particles are estimated using procedures we have previously evaluated^{1,2}.

Chemistry

AROSOL offers two options in the calculation of the homogeneous gas phase conversion of SO_2 to sulfate. One of these is an empirical first-order decay model due to Meagher¹¹. The other is a complex photochemical mechanism known as the carbon bond mechanism (CBM)¹²

suitably modified for sulfate conversion. The empirical model will be discussed first.

Empirical Model--

The empirical model of Meagher¹¹ (EMM) is based on field measurements. Its simplicity and computational efficiency make it appealing for first-order estimates of sulfate formation rates when the amount of reliable input data is limited. This model will be used first in our model studies with AROSOL with available urban data bases such as RAPS and the 1982 Philadelphia data from PAFS.

EMM is based loosely on the diurnal and annual variation in clear-sky solar intensity. The basic assumption is that the rate constant for sulfate conversion can be separated into a constant value and a component that is allowed to vary diurnally and annually. Thus the rate constant for any particular time of day and any day of the year can be estimated using the following equation:

$$k(t,i) = k_0 + k_{\max} f_A(i) f_D(t) \quad (1)$$

where

$k(t,i)$ = the diurnally and annually varying rate constant

t = time of day (solar)

i = Julian date

k_0 = the time invariant component of the rate constant

$k_{\max}$ = the maximum value of the time varying portion of the rate constant

$f_A(i)$ = a function describing the annual variations in the daily, time invariant maximum

$f_D(t)$ = a function describing the diurnal change in the time variant portion of the rate constant

the various parameters in eq.(1) were established from empirical analysis of 12 field studies and from solar studies by Duffie and Beckman¹³, who reported the following equation for day length, T_d :

$$T_d = 0.133 \cos^{-1} - \tan L \tan D$$

where

L = latitude (degrees-north positive)

D = declination-degrees (angle of sun at solar noon with respect to the plane of equator)

A combination of the diurnal and seasonal functions provides the following equation for the pseudo first order rate constant, $k(i,t,T_d)$:

$$k(i,t,T_d) = 0.002 + 0.006625(\cos(2p(i-192.5)/365) + 1) \times (\cos(2p(t-12)/T_d) + 1) \quad (2)$$

where $k(i,t,T_d)$ is in units of hours^{-1} .

Meagher¹¹ found that eq.(2) accounts for 56 percent of the observed variation in 103 individual field measurements of this rate constant. EMM was derived from a consistent set of data from multiple field studies conducted in each of four seasons to optimize its parameters. The model was formulated to give an average over these field results and it cannot be supposed that it will exhibit skill in reproducing individual events. It will be predictive only insofar as events to be modeled with it are within the same reactive regimes. The field studies used for derivation of EMM represent on the whole rural conditions. Therefore, EMM must be applied

with caution in our urban simulations; results from its use are to be regarded as guides in carrying out simulations with the more complex and expensive CBM.

CBM-IV mechanism--

The carbon bond mechanism (CBM) approach¹⁴ appears to be an attractive method for modeling atmospheric organic chemistry and therefore, suitably modified, appears to be useful in modeling sulfate conversion. In the CBM, organic species are grouped according to type and number of carbon bonds in the molecule irrespective of the particular chemical species in which the bond is found. The structural classes have been determined through the use of structural reactivity analysis. The lumping of organic species in the CBM becomes transparent if one examines the scheme for CBM-IV shown in Table 1 below.

The carbon bond mechanism has several advantages over other lumped mechanisms. To name a few, it conserves carbon atoms, it has a narrow range of reactivities for a group of lumped species, and the reactivity of the organic mixture changes in a natural way. The mechanism follows the reactions of the lumped species. The rate constants for these species are obtained by averaging the rate constants for the individual species that comprise the lumped identity. The reactivity of an organic mixture changes according to the concentrations of the different bond types in the carbon mechanism.

CBM uses a hierarchy of chemical species in which each species involved in oxidant formation is assigned a hierarchical level on the basis of the number of systems in which it occurs. This is illustrated schematically in the figure below.

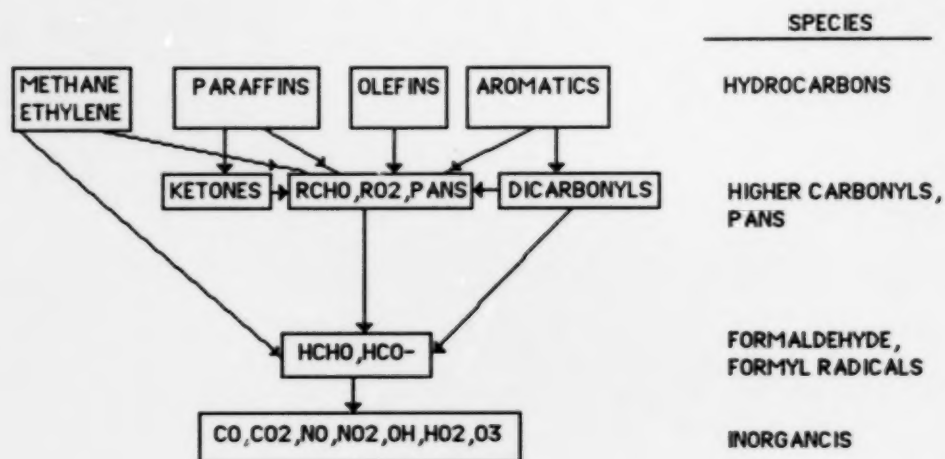


FIGURE 1. Schematic diagram of hierarchical levels of chemical species in photochemical smog (after reference 14).

AROSOL includes CBM-IV which is a condensed version of the larger CBM-X mechanism. This condensed version is suitable for use in a computationally demanding model such as AROSOL in an urban or regional area.

Table 1 contains the version of CBM-IV that is currently used in EPA's Regional Oxidant Model supplemented with a sulfate formation mechanism that excludes the reactions of the Criegee intermediates. The Criegee intermediates, which can react with NO_x, H₂O and SO₂ would only be important when the hydrocarbon to nitrogen oxides ratio is very large and at the same time the relative humidity is very low; these conditions are not thought to be common in urban areas. The photolytic reactions are #s 1, 8, 9, 19, 24, 28, 33, 34, 40, and 47. The rates of most of these reactions are known to vary with zenith angle in a fashion similar to the photolysis of NO₂. Therefore, the rate constants for these reactions are expressed as a multiple of the photolytic constant for NO₂. The

photolysis of O_3 to $O(^1D)$ (reaction #8) and the photolysis of formaldehyde and acetaldehyde (reactions 33, 34, and 40) vary with zenith angle in a manner dissimilar to that of NO_2 , and they are therefore treated differently in the mechanism. EPA is now revising the treatment of these reactions. In addition to the revision of the treatment of the photolytic species, EPA is also modifying the chemistry used to represent ethylene and the aromatics. All these revisions are due to be completed this summer. Reactions 71 to 75 are added to account for photochemical conversion of SO_2 after the scheme proposed by Meagher¹¹. Table 2 interprets the symbols used in Table 1.

It is not necessary to treat all of the reactions listed in Table 1 as differential equations. The fast reactions may be reduced to algebraic equations by the quasi-stationary state assumption. This has the advantage of reducing the stiffness of the set of differential equations represented by Table 2. With the quasi-stationary state assumption the rate equations derived from the reactions of Table 1 become a set of mixed algebraic and differential equations. We have had considerable experience with the solution of such mixed sets. At present we use LSODI from the Lawrence Livermore National Laboratory modified to solve the set of mixed equations indicated.

Up to now we have not mentioned an important problem in modeling atmospheric chemical reactions such as shown in Table 1. This is the fact that these reactions occur in a turbulent environment. This problem is well known^{e.g. 15,16} and poses obvious difficulties in applying first order closure to second order reactions when the characteristic reaction times are much less than the Lagrangian time scale of the turbulence. For regional scale models when concentration levels of reactants are low, these considerations may be less important than for urban scale models near sources. Accounting for correlation effects on the chemical reaction rates will require sub-grid scale modeling, a subject now under study for AROSOL.

CARBON BOND MECHANISM -- IV FOR ALFATE

Reactions	Rate Const.	Activation Energy
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1	NO2	= NO + O	VARY	
2	O	= O3	4.65E6	-690.
3	O3 + NO	= NO2	26.6	1430.
4	O + NO2	= NO	13800.	
5	O + NO2	= NO3	2320.	-600.
6	O + NO	= NO2	3120.	-411.
7	NO2 + O3	= NO3	0.0474.	2450.
8	O3	= 0.205 OH + 0.897 O	VARY	
9	O3	= O	0.0421xk1	
10	O3 + OH	= HO2	100.	940.
11	O3 + HO2	= OH	3. 580.	
12	NO3 + NO	= 2 NO2	28100.	-250.
13	NO3 + NO2	= NO + NO2	0.59	1230.
14	NO3 + NO2	= N2O5	1780.	60.
15	N2O5	= 2 HNO3	0.0285	
16	N2O5	= NO3 + NO2	3.12	10840.
17	NO + NO2	= 2 HNO2	2.4E-7	
18	HNO2 + HNO2	= NO + NO2	1.5E-5	
19	HNO2	= NO+ OH	0.18xk1	
20	NO2 + OH	= HNO3	16300.	-560.
21	NO + OH	= HNO2	9770.	-427.
22	HO2 + NO	= OH + NO2	12300.	-240.
23	NO + NO	= 2 NO2	1.52E-4	-530.
24	H2O2	= 2 OH	.0014xk1	

25	OH + H2O2	= HO2	2520.	187.
26	OH + HNO2	= NO2	9770.	
27	OH + HNO3	= NO3	192.	-778
28	NO3	= 0.85NO2 + 0.85O + 0.15NO	30.6xk1	
29	HO2 + HO2	= H2O2	4144.	-1150
30	HO2 + HO2	= H2O2	3270.	-5800.
31	OH + CO	= HO2	400.	
32	FORM + OH	= HO2 + CO	15000.	
33	FORM	= 2HO2 + CO	VARY	
34	FORM	= CO	VARY	
35	FORM + O	= OH + HO2 + CO	237.	1550.
36	FORM + NO3	= HNO3 + HO2 + CO	0.93	
37	ALD2 + O	= C2O3 + OH	636.	986.
38	ALD2 + OH	= C2O3	24000.	-250.
39	ALD2 + NO3	= C2O3 + HNO3	3.7	
40	ALD2	= XO2 + 2HO2 + CO + FORM	VARY	
41	ALD2 + HO2	= XO2 + 2 FORM + HO2	5.	
42	C2O3 + NO	= NO2 + XO2 + FORM + HO2	16500.	-250.
43	C2O3 + NO2	= PAN	9000.	-250.
44	PAN	= C2O3 + NO2	0.0222	14000.
45	C2O3 + C2O3	= 2XO2 + 2FORM + 2HO2	3700.	
46	C2O3 + HO2	=	9600.	
47	MGLY	= C2O3 + HO2 + CO	0.02xk1	
48	MGLY + OH	= XO2 + C2O3	26000.	
49	OH	= XO2 + FORM + HO2	21.	
50	PAR + OH	= 1.49XO2 + 0.067XO2N + 0.93HO2 + + 0.45ALD2 - 0.75PAR	1150.	
51	O + OLE	= 0.95ALD2 + 0.35HO2 + 0.2XO2 + 0.15CO + 0.05FORM + 0.05C2O3 + -0.35PAR	5920.	324.
52	OH + OLE	= FORM + ALD2 + XO2 + HO2 -PAR	42000.	-537.

53	O3 + OLE	= 0.5ALD2 + 0.66FORM + 0.212CO + 0.28HO2 + 0.144XO2 + 0.08OH- PAR	0.018	1897.
54	NO3 + OLE	= 0.91XO2 + 0.91HO2 + 0.09XO2N	11.4	
55	O + ETH	= FORM + XO2 + CO + 2HO2	1080.	800.
56	OH + ETH	= XO2 + 2FORM + HO2	12000.	-382.
57	O3 + ETH	= FORM + 0.37CO + 0.13HO2	0.0027	2840.
58	TOL + OH	= HO2 + 0.64XO2 + 1.13FORM + 0.56MGly + 0.36PHEN+ 0.36PAR + 1.13CO	9750.	
59	PHEN + NO3	= PHO + HNO3	14000.	
60	PHO + NO2	=	20000.	
61	XYL + OH	= HO2 + 0.72XO2 + 0.67CO + 1.33MGly + 0.28PHEN + 0.56PAR + 0.06TLA + 0.67FORM	36000.	
62	TLA + OH	= XO2 + PHO + 2PAR	20000.	
63	ISOP + O	= HO2 + 0.8ALD2 + 0.55OLE + 0.5XO2 + 0.5CO + 0.45ETH -0.1PAR	28000.	
64	ISOP + OH	= 0.87XO2 + 0.87FORM + 0.87HO2 + 0.29PAR + 0.29OLE + 0.58ETH + 0.29ALD2	126000.	
65	ISOP + O3	= FORM + 0.45ALD2 + 0.55ETH + 0.98HO2 + 0.10LE + 0.06CO -0.25PAR	0.018	
66	ISOP + NO3	= XO2N	165.	
67	XO2N + NO	=	1000.	
68	XO2 + NO	= NO2	12000.	
69	XO2 + HO2	=	5000.	-1300.
70	XO2 + C2O3	= XO2 + NO2 + FORM	2400.	

71	HO + SO2 +(O2,H2O) = HO2 + H2SO4	1496.
72	HO + SO2 +(O2)	= HSO5 23.
73	HSO5 + NO = NO2 + HSO4	10268.
74	HSO4 + HO2 = H2SO4 + O2	256.
75	HSO4 + O3 = HSO5 + O2	10.

Rate constants in ppm min units at 298K. Activation energies are B in expression

$$k_T = k_{298} \exp(B(1/298 - 1/T)).$$

TABLE 2 . SPECIES USED IN MODIFIED CBM-IV MECHANISM

<u>Mechanistic symbol</u>	<u>Name</u>
NO	NITRIC OXIDE
NO2	NITROGEN DIOXIDE
NO3	NITROGEN TRIOXIDE
N2O5	DINITROGEN PENTOXIDE
HNO2	NITROUS ACID
HNO3	NITRIC ACID
O	ATOMIC OXYGEN (O3P)
O3	OZONE
OH	HYDROXYL RADICAL
HO2	HYDRO PEROXY RADICAL
CO	CARBON MONOXIDE
H2O2	HYDROGEN PEROXIDE
PAN	PEROXYACYL NITRATE
FORM	FORMALDEHYDE
ALD2	ACETALDEHYDE
MGLY	METHYL GLYOXAL
PAR	PARAFFIN CARBON BOND
OLE	OLEFIN CARBON BOND
ETH	ETHYLENE
TOL	TOLUENE SURROGATE
XYL	XYLENE SURROGATE
TLA	TOLUALDEHYDE SURROGATE
ISOP	ISOPRENE
C2O3	PEROXY ACYL RADICAL
PHEN	PHENOL (CRESOL) SURROGATE
PHO	PHENOXY RADICAL SURROGATE
XO2	PEROXY RADICAL
XO2N	PEROXY NITRATE
HSO4	HYDROGEN SULFATE FREE RADICAL

HSO5
H2SO4

HYDROXYSULFATE FREE RADICAL
SULFURIC ACID

Aerosol dynamics

The term aerosol dynamics in the present context refers to the processes of nucleation, condensation, evaporation, and coagulation¹⁵. These processes alter the size and composition distributions of the ambient atmospheric aerosol. The eventual need for knowledge of these distributions in the regulatory process has been discussed briefly in Section 1. Apart from this, knowledge of the aerosol dynamics is essential to a basic understanding of the complex atmospheric and chemical processes and their effects involved in atmospheric pollution.

There are two limits in the approach to modeling secondary aerosol formation in the atmosphere. An illustration will serve to make these limiting approaches clear.

For the case of sulfate conversion considered in this report, most regional models regard sulfate as essentially another chemical species and take no account of its distribution in size and composition; in this approach, termed here the lumped aerosol model (LAM), sulfate is emitted from primary sources, created by atmospheric reactions, advects and disperses, and undergoes deposition processes in an analogous manner to gaseous species. It is in the treatment of the deposition processes that one of the deficiencies of this approach becomes apparent. Deposition processes for sulfate particles are size and possibly composition dependent; therefore, in order to be generally useful, empirical formulations of such deposition rates must erroneously assume a universal distribution of sulfate.

At the other extreme is the model that deals with particle size and composition distributions and attempts to account for all the aerosol dynamics processes--an approach termed here the aerosol dynamics model (ADM). This may be styled as an *ab initio* approach, which at least in principle is not required to invoke any empirical rate information.

AROSOL has the option of invoking either the LAM or ADM. The LAM option would be suitable for some assessment purposes, where, for example, sulfate mass concentration would be the only interest. It is one of the

aims of this project to compare the LAM and ADM options in urban simulations with AROSOL. This is now possible with the University of Texas CRAY-XMP . The LAM and ADM options as they exist with AROSOL will now be discussed.

Lumped aerosol model (LAM) --

As usually applied, LAM deals with the mass concentration of sulfate as another chemical species. The rationale for this approach has been shown explicitly². The contributions to the rate processes for sulfate mass concentration may be indicated schematically:

rate of change of sulfate

$$\begin{aligned} \text{mass concentration} &= (1) \text{ (rate of change due to advection)} \\ &+ (2) \text{ (rate of change due to dispersion)} \\ &+ (3) \text{ (rate of change due to sedimentation)} \\ &+ (4) \text{ (rate of change due to deposition)} \\ &+ (5) \text{ (rate of change due to condensation)} \\ &+ (6) \text{ (rate of change due to homogeneous nucleation)} \end{aligned}$$

It may be noted that the coagulation process does not enter since the sulfate mass concentration is conserved by coagulation; coagulation does not alter the mass concentrations, but merely changes the composition distribution. It is always observed in atmospheric aerosol simulations that particles less than the order of 2 micrometers evolve independently of the larger particles and that particle growth processes arising from homogeneous nucleation, condensation and coagulation do not affect the larger particles². Therefore, the sulfate mass concentration may be regarded as being made up of two independent fractions: particles greater than approximately 2 micrometers produced by primary sources and those smaller, the so-called "fine particles" that arise both from primary source

input and secondary sources. Sedimentation is unimportant for the fine particle fraction. It is in consideration of rate processes 4,5 and 6 that the deficiency of the LAM approach is manifest. Deposition and condensation rates are directly dependent on particle size. A deposition rate must be obtained empirically for sulfate to close the sulfate mass conservation equation; however, this deposition rate will be dependent on the size distributions existing during the field measurements and may not be applicable at other locations or times. In the LAM approach, the distinction between condensation and homogeneous nucleation is ignored. If heterogeneous conversion processes are negligible, the rate of formation of particulate sulfate mass concentration is assumed to be equal to the rate of production of vapor phase sulfate mass concentration by chemical reaction. Since the sulfate species produced have very low vapor pressures, this assumption appears to be acceptable. Such an assumption may not be valid for more volatile components of the atmospheric aerosol such as the nitrates and some of the organic fractions. Of course, if one is interested in sulfate moments of the composition distribution other than the mass, the LAM approach becomes more questionable. For example, it becomes more difficult to justify the LAM approach in modeling phenomena more sensitive to the composition distribution, such as light scattering and absorption.

From this discussion, it would appear that if one is interested solely in the sulfate mass concentration, the LAM approach is useful, although there will always remain the uncertainties in the deposition rate processes. However, these uncertainties are not trivial; many of the adverse effects of particulate sulfate are associated with the deposition of the particulate sulfate--in the lung, on leaves, or on water or ice surfaces.

The ADM approach will be necessary to model such effects.

Aerosol dynamics model (ADM) --

A large part of this project has been concerned with developing the ADM

approach. We have developed accurate and efficient numerical schemes for simulation of coagulation and condensation/evaporation processes^{17,18,19,20,21} and have carried out the first comprehensive studies^{e.g.22,23,24} of aerosol growth in the context of a model for atmospheric dispersion and transport. The modules for coagulation and condensation/evaporation that have been developed have proven to yield accurate simulations of aerosol growth processes in the atmospheric models. These modules have provided the reference calculations for evaluation of more approximate calculation schemes²⁵. All this work has been done for aerosol dynamics models for the particle size or mass distribution, $n(m,r,t)$, where $n(m,r,t)dm$ is the number of particles having masses in the range m to $m+dm$ at a vector position in space, r , at time t .

Current work on ADM is directed toward extension of the accurate modules to multicomponent aerosol dynamics and to development of approximate but computationally efficient methods, which can be checked with calculations using the accurate modules.

The development of accurate multicomponent aerosol dynamics modules is now facilitated with the availability of the CRAY -XMP at the University of Texas Center for High Performance Computing. This work will be reported in the near future.

We have shown that accurate numerical methods are available for simulation of aerosol dynamics, including the evaporation process. However, these accurate methods may not be feasible for many spatially inhomogeneous, unsteady state problems, for which computer time can be prohibitive, even on current supercomputers. In addition, even for computationally feasible problems, it is desirable to have available numerical techniques that are easily and rapidly applied. Of these approximate techniques, the moment method appears most promising. Earlier work on the use of the moment method for solution of the coalescence equation has been reviewed by Drake²⁶. Clark²⁷ reported results on numerical calculations of the cloud physical equations of condensation and coalescence theory using both lognormal and gamma distributions to effect

closure of the moment equations. More recently, the moment method with closure by the lognormal distribution has been widely applied in analysis of aerosol dynamics^{28,29,30}. We have recently extended for the first time the moment method to the aerosol evaporation problem; this extension appears capable of providing reasonably accurate simulations of atmospheric aerosol evaporation.

In the ADM approach, the aerosol growth processes are incorporated in a general atmospheric transport and dispersion model. Reynolds averaging may be carried out in the usual way and, for first order closure, one obtains the K-theory representation of atmospheric transport and dispersion with suitable averages for the aerosol rate processes; these averages are acceptable provided the characteristic time scales for the aerosol rate processes are much greater than the Lagrangian time scale of the turbulence. The situation here is the same as discussed above in the section on atmospheric chemistry. The relation of aerosol growth processes to turbulent fluctuations has been discussed³¹. With these assumptions, for a single component aerosol, in ADM one studies the evolution of the particle number density function $n(m, x, y, z, t)$ defined above according to the conservation equation, where only the flat terrain formulation is given for brevity:

$$\begin{aligned} \frac{dn(m, x, y, z, t)}{dt} + U(z) \frac{dn(m, x, y, z, t)}{dz} + \frac{d[f(m, s) n(m, x, y, z, t)]}{dm} \\ = \frac{d(K(z) \frac{dn(m, x, y, z, t)}{dz})}{dz} + \frac{d(K(y) \frac{dn(m, x, y, z, t)}{dy})}{dy} \\ + G_z \frac{dn(m, x, y, z, t)}{dz} + \frac{1}{2} \int_0^\infty b(m-m', m') n(m-m') n(m') dm' \\ - n(m) \int_0^\infty b(m, m') n(m') dm' + R \end{aligned} \quad (3)$$

This equation is coupled to the following conservation equation for the vapor making up the particle, given in terms of the saturation ratio, s :

$$ds(x,y,z,t) / dt + U(z) ds(x,y,z,t) / dx \quad (4)$$

$$= d(K(z) ds(x,y,z,t) / dz) / dz + d(K(y) ds(x,y,z,t) / dy) / dy$$

$$-(1/c_v) \int_0^\infty f(m,s) n(m,x,y,z,t) dm - (1/c_v) m^* R + S$$

These equations are subject to the usual boundary and initial conditions -- zero flux condition at the mixing height, $z=H$, constant flux conditions at the horizontal boundaries, and the usual deposition velocities at the surface. Again, for the flat surface formulation for brevity, the deposition velocities have the form:

$$nV_d(m) = -K(z)dn/dz - G_z n, \quad z = 0 \quad (5)$$

$$sV_d(s) = -K(z)ds/dz, \quad z = 0$$

In these equations, $U(z)$ is the x component of the mean fluid velocity, and $K(z)$ is the vertical and $K(y)$ the transverse eddy diffusivities; $G_z(m)$ is the gravitational settling speed for a particle of mass m . $V_d(m)$ is the deposition velocity of a particle with mass m and $V_d(s)$ that for the vapor at saturation ratio, s . f is the condensation and evaporation growth law for a particle. $b(m,m')$ is the coagulation coefficient. R is the homogeneous nucleation rate, c_v the vapor mass concentration, m^* the critical nucleus mass, and S is the chemical conversion source term. These equations represent integration over the multicomponent aerosol evolution equations for $n(m,x_1,x_2,\dots,x_c)$ where $x_1,x_2,\dots,x_c$ are mass fractions of the c species in the aerosol. From this viewpoint, the growth rates such as f , R , and S must be regarded as rates averaged over the various chemical species.

The accurate numerical techniques for calculation of the rate processes of coagulation and condensation/evaporation have been referenced above and are summarized in an EPA report³². A comparison of some approximate techniques with these accurate methods has been referenced above²⁵. Accurate numerical techniques have been studied with the time splitting procedure for the solution of condensation/evaporation and coagulation with advection and dispersion according to the equations above with the deposition boundary conditions. Therefore, in principle, the ADM approach can now be carried out for atmospheric aerosol modeling for the singlet density function $n(m,r,t)$. The principal difficulty in carrying out such calculations lies in the lack of suitable field data for evaluation of the modeling procedures; suggestions for resolving this difficulty have been discussed briefly in the Recommendations, Section 3.

Recently, we have developed a moment technique³⁰ for solution of the aerosol evolution equation including condensation and homogeneous nucleation in single component aerosol and have shown in this study that the method yields results in reasonable comparison with experimental measurements. In as yet unpublished work, we have extended the moment method to the evolution of a binary aerosol evolving by binary condensation and binary homogeneous nucleation. Separately, we have extended this moment technique to obtain reasonably accurate simulations of the evolution of a single component evaporating aerosol³³; the method is readily extended to multicomponent aerosol. The moment techniques employed in all these studies are computationally efficient and promise to make it feasible to carry out numerical simulations of the multicomponent aerosol generalizations of equations 3 and 4 above.

Again, the way is now open computationally to carry out simulations of multicomponent atmospheric aerosol; however, suitable field data are lacking for evaluation of the results from such model studies.

SECTION 5

RESULTS AND DISCUSSION

The work reported here details recent modifications to AROSOL, an urban scale K-theory model for the urban aerosol. The principal modification is the addition of two modules for the conversion of SO₂ to sulfate. One of these is based on the empirical model of Meagher¹¹ (EMM) and the other on the carbon bond mechanism (CBM) in the so-called version IV. Details of these models have been given in Section 4. In addition to this modification, the modules in AROSOL for calculation of advection and vertical diffusivity have been updated to reflect advances in the numerical treatment of these processes. Also, exact and approximate methods have been tested for simulation of aerosol coagulation, condensation and evaporation, and both unary and binary homogeneous nucleation. These methods are available as modules for AROSOL.

The first evaluation of AROSOL for urban sulfate simulation is to be carried out using the results of the 1982 Philadelphia Aerosol Field Study (PAFS) sponsored by EPA to obtain detailed data bases on emissions and surface air concentrations of gases and particles, and concurrent meteorological conditions. This study was designed to obtain adequate temporal and spatial resolution to evaluate source and receptor models, including AROSOL, for short term simulation of urban aerosol, with particular emphasis on prediction of secondary sources of the urban sulfate aerosol. Philadelphia was selected for this study because it has a variety of industrial sources and it was the site of an earlier field study for evaluation of EPA's Urban Airshed Photochemical Oxidant model.

PAFS was carried out from July 14 to August 14, 1982. From the data collected, a data base has been prepared by EPA including emission inventories, meteorological data, and gas and particulate concentrations. These data have been incorporated into AROSOL by procedures described in Section 4. An evaluation of AROSOL including EMM and CBM-IV is now being

carried out. The results of this evaluation will be detailed in a forthcoming report due under the current contract. Here we report only a few results from our preliminary tests of EMM using a portion of the PAFS data base; CBM-IV is now under modification by EPA and the revisions should be available this summer when tests of the CBM-IV module will be made.

Preliminary tests of AROSOL using EMM were carried out by "switching on" only the two largest SO₂ sources in the study area. These are the Philadelphia Electric Company Eddystone and Cromby plants. The study area in elevation is shown in Figure 1. The area extends well beyond the monitoring stations to the West and South and includes all of Philadelphia County to the North and East. With this arrangement, all of the emissions data important for model evaluation are included in the study area. Stability classes D and E were simulated for the meteorological conditions for 3 August 1982 of the study. The results for SO₂ and secondary sulfate for D class stability are shown in Figures 2 and 3. The values for D class stability are for 0500 hours. Similar results for E class stability are shown in Figures 4 and 5 at 0100 hours.

As can be seen from these simulations, the isopleths in Figures 2 - 4 are non-Gaussian in form. The two large sources of SO₂ represented in Figures 2 - 4 will dominate the downwind concentration fields of SO₂ and secondary sources. This is a source of difficulty in all model evaluation studies, since small (5%) variation in the wind direction can cause large discrepancies between simulated and measured values at the sampling locations. We plan to investigate a statistical approach to resolving this difficulty by determining, where possible, a probability density for the variation in the wind vector. In addition, we will estimate, where possible, similar densities for the large sources in the emissions inventory. By such analyses, one can attempt to assign certain probabilities to the variation between simulated and measured values.

The simulations reported above represent application of the lumped aerosol model (LAM) for sulfate. The deficiencies associated with LAM have

been discussed in some detail in Section 4. In the case of the PAFS data base, it may be argued that the detail afforded by the more rigorous approach of the aerosol dynamics model (ADM) cannot be examined through the data base; no information on the size or composition distributions of the aerosol is contained in the data base. In our evaluation studies, we only plan to carry out comparisons of LAM with ADM results to examine the deficiencies noted above in LAM for the urban aerosol.

Simulation using ADM now appears to be possible for multicomponent aerosol using the moment techniques we have developed. These techniques permit solution of the multicomponent aerosol evolution equation including nucleation, condensation and coagulation. In the third year of our study, secondary nitrate and organics will be included in the ADM simulations. With the availability of the University of Texas CRAY-XMP, it will be possible to carry out the ADM simulations using the CBM-IV chemistry module with AROSOL.

A subject for investigation is the possibility of developing from AROSOL a simplified model suitable for assessment purposes. There is no serious debate on the inadequacies of the current practice of Gaussian plume modeling. Gaussian plume modeling can only be defended now on the basis of economic arguments that large mainframes are necessary to run K-theory models such as AROSOL and that this requirement places K-theory models beyond the economic capability of various interests. This picture, however, is changing rapidly with the advent of relatively inexpensive computer workstations with virtual memory and RISC (reduced instruction set computer) architecture. It seems appropriate to begin now to examine the possibility of developing simplified K-theory models that will run on such workstations. One to two years from now, the performance of such workstations may in any case be comparable to some present mainframes. IBM has recently started marketing the IBM PC-RT which has a price range from \$13,000 to around \$30,000, depending on the peripherals and disk storage. The RT may be available to us from IBM's Project Quest and we plan to explore porting AROSOL to the RT through "engineering" model development

and special coding for the RT.

The simplified model development is proceeding along several lines. Most significantly, we are exploring the degradation in accuracy by choosing larger time steps and larger spatial grids. Problems arising from larger spatial grids in modeling point sources are to be resolved through automatic introduction of subgrids where necessary. The AROSOL code is in any event being vectorized for use on the CRAY-XMP and this will be of advantage for the simplified model should coprocessors be available.

With respect to the IBM PC-RT, two principal features will be explored. The first is how to deal with the very large in-data requirements of the code in the context of the RT. The second is how the code needs to be modified or enhanced in order to allow it to run in a reasonable time on the RT. In connection with the second feature, it may be suitable for the code running time to be of the order of an hour ; this may require significant changes in the code and push the RT to its limits in speed. All usage will probably require some kind of graphical display of the results and this code will be developed solely on the RT.

The RT possesses a number of advantages for porting the "engineering" model:

- 1) For the purposes anticipated, the various interests of necessity require only a small relatively cheap machine for their purposes -- hence the choice of a personal workstation or PC.
- 2) The code requires virtual memory assistance which the RT provides. Currently, the memory limit on even many mainframes places severe restrictions on the size of the model which can be run on such mainframes; the RT has no such limitations.
- 3) The time consideration requires a fast processor. IBM's RISC architecture provides this speed. Rewriting some parts of the code in assembler language so as to take advantage of this may result in a significant improvement in performance.

In summary, porting a K-theory code such as AROSOL to a computer workstation such as the RT will provide a significant advance. A number of advantages would follow from this development. For example, the K-theory model is a significant innovation for the wide-spread applications

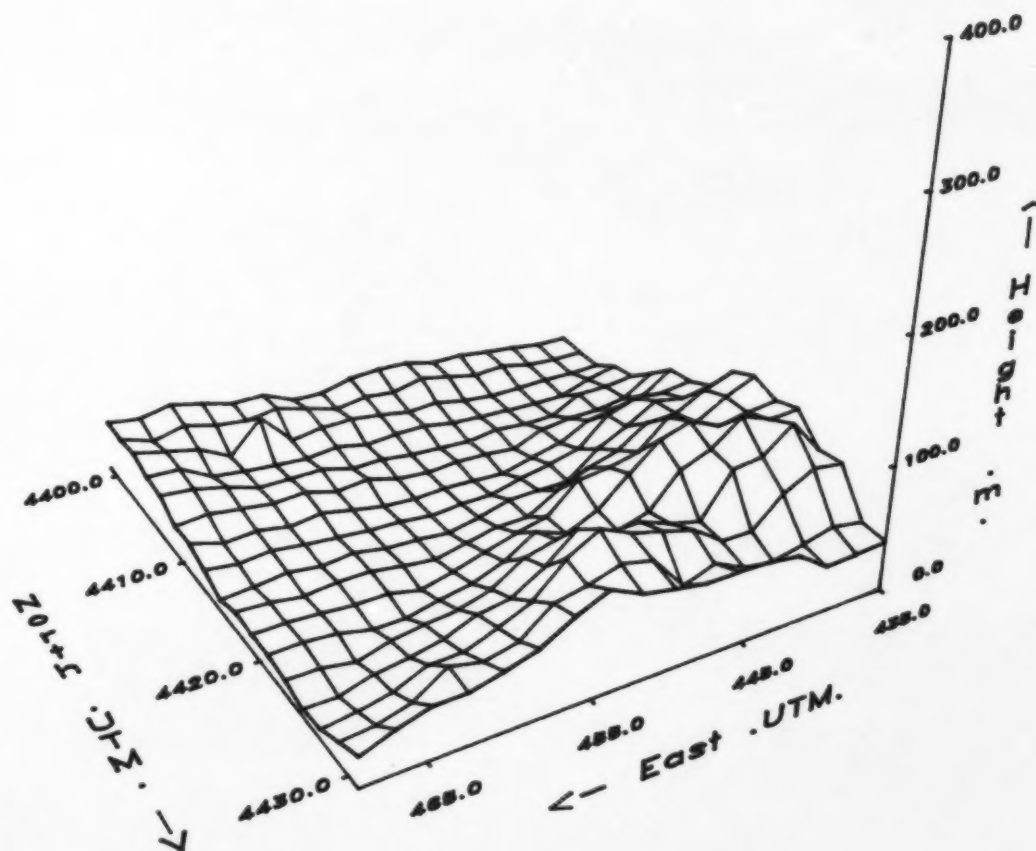
envisioned. A comparison of how the large data requirements can be handled on a fixed memory limit machine and hardware assisted virtual memory machine will give some information as to the usefulness of the RT for such purposes as this model. Finally, this will provide an exploration of the extent to which RISC architecture can be made use of in improving performance of such models.

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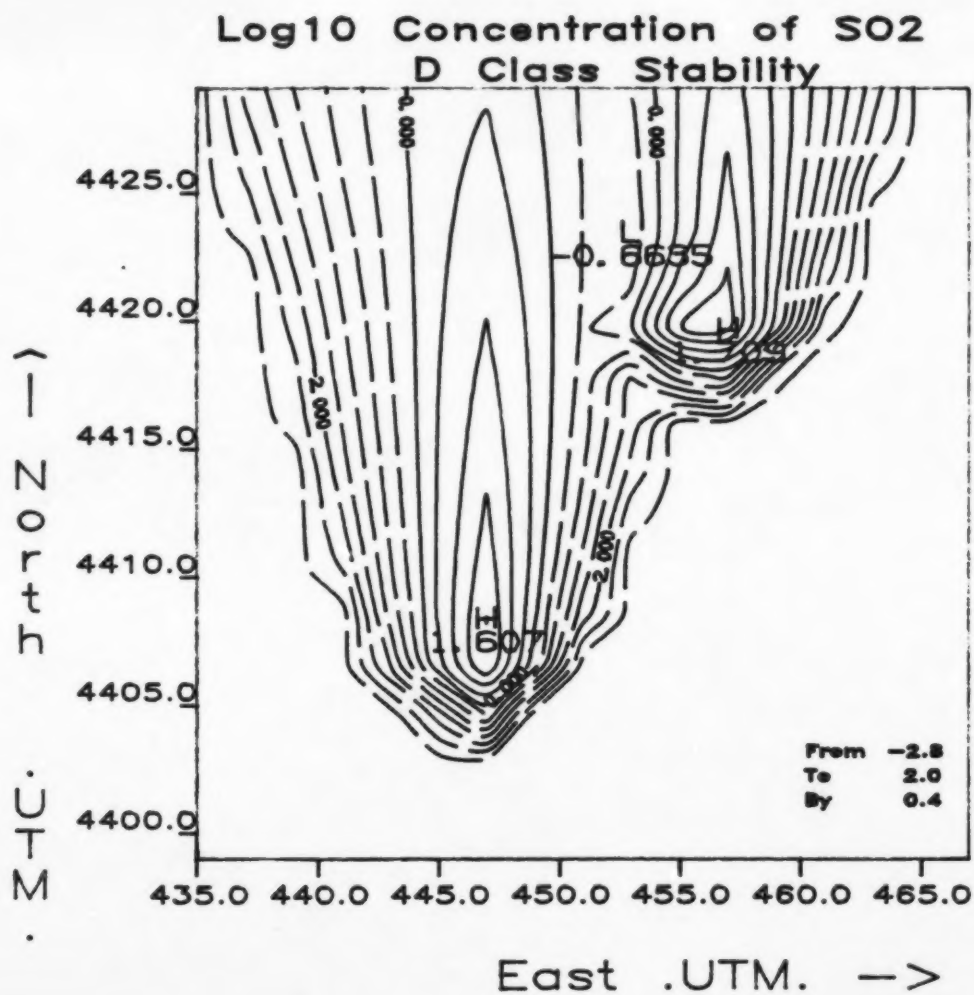
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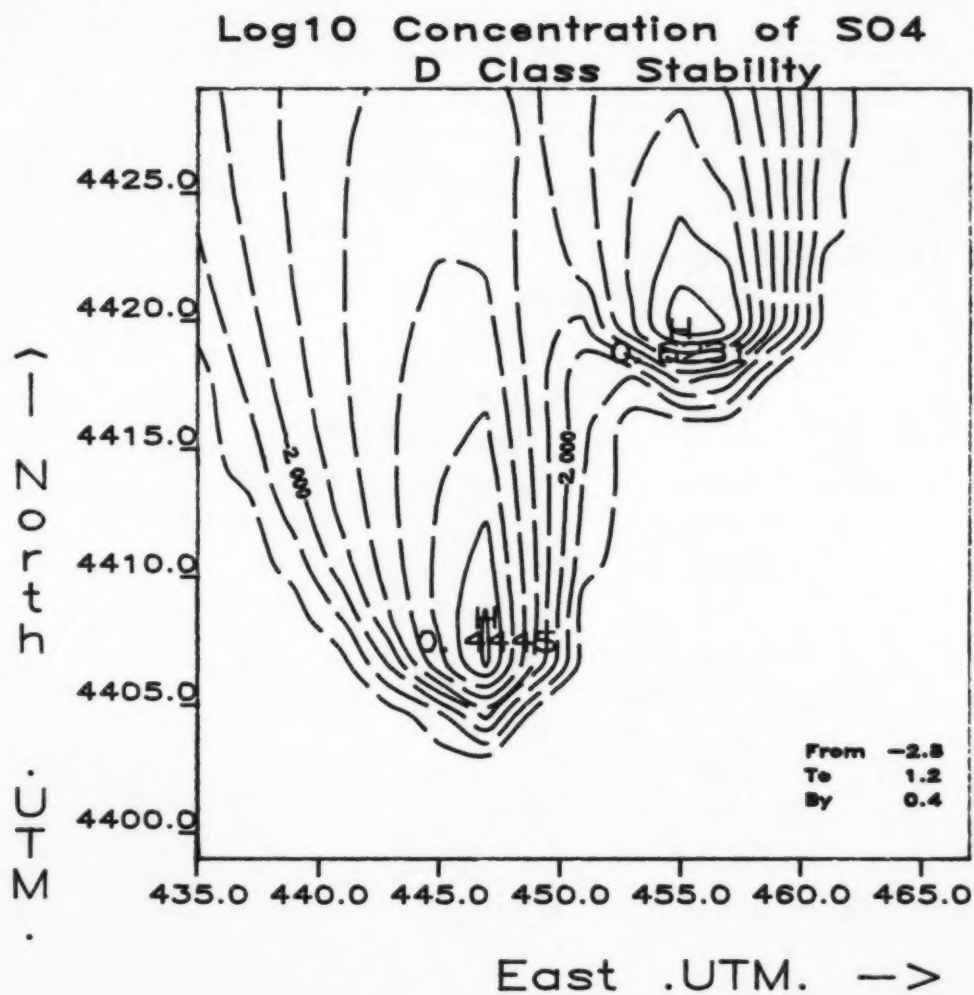
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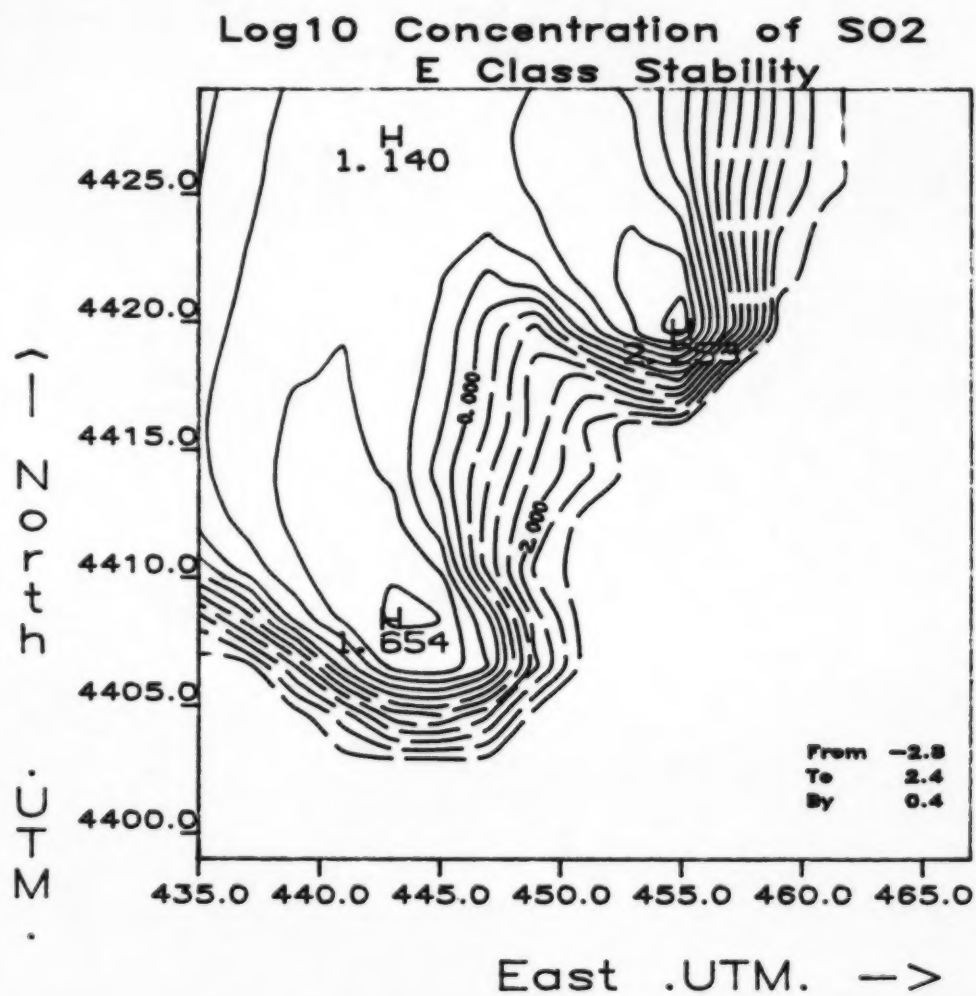
No. 1. Terrain in study area for 1982 Philadelphia Aerosol Field Study data base.



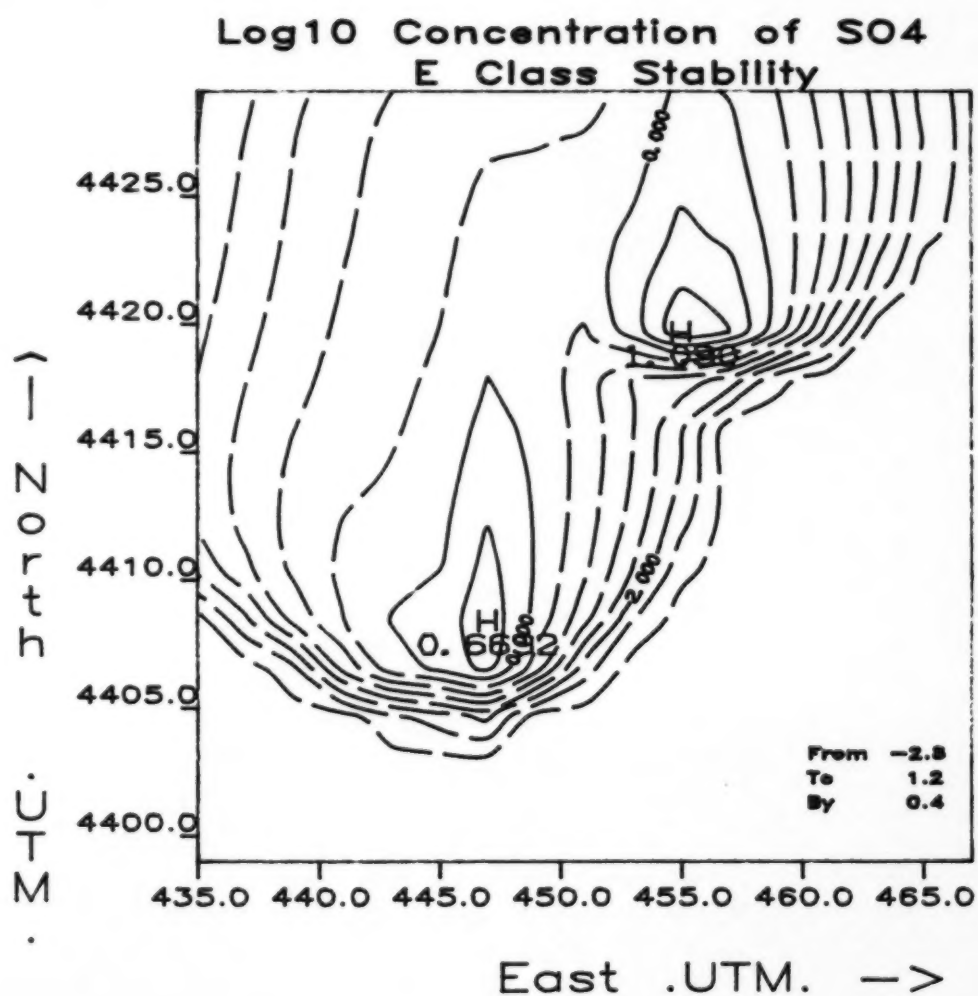
No. 2. SO₂ distribution given by AROSOL simulation from two largest sources in study area for D class stability.



No. 3. Secondary sulfate distribution given by AROSOL simulation with EMM in study area for D class stability.



No. 4. SO₂ distribution given by AROSOL simulation from two largest sources in study area for E class stability.



No. 5. Secondary sulfate distribution given by AROSOL simulation with EMM in study area for E class stability.